AIR QUALITY DRYDEN

Annual Report 1975

Ontario Ministry of the Environment

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AIR QUALITY
DRYDEN

ANNUAL REPORT, 1975

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NORTHWESTERN REGION
ONTARIO MINISTRY OF THE ENVIRONMENT

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SUMMARY

Air quality investigations by Ontario Ministry of the Environment began in Dryden in 1970 to assess effects on local environment of emissions from a kraft pulp mill and mercury-cell chlor-alkali plant operated by Dryden Paper Company Limited and Dryden Chemicals Limited, respectively (now Reed Limited). Assessment surveys have included vegetation, soil and snow sampling and ambient air monitoring.

Mercury concentrations were elevated in vegetation and soil in the vicinity of the chlor-alkali plant and pulp mill, and decreased with increasing distance from these facilities. Similar trends were less clear for chloride and sodium in local vegetation and soil. Snow sampling, however, showed well defined patterns of contamination by calcium, sodium and sulphate up to 1500 metres from the mill area. Mercury levels in snow were also elevated in a small zone on and near company property. Atmospheric mercury concentrations were elevated at several sites in Dryden, but the Ontario standard was not exceeded. Values slightly above the standard were recorded at the company's mercury disposal site about 5 kilometres west of Dryden.

Insufficient dustfall samples were collected to establish any trend or to establish whether Ontario criteria were being frequently exceeded. Limited sampling of suspended particulate indicated that above-criteria values were fairly common. Sulphation rates, over a 3-month period, indicated the presence of hydrogen sulphide contamination. Further evidence of a hydrogen sulphide problem was obtained from ambient air monitoring, which recorded levels of hydrogen sulphide well above the Ontario standard at many points in the town area. Sulphur dioxide concentrations were very low.

INTRODUCTION

The principal industrial source of air pollution in Dryden is a 625 ton per day bleached kraft pulp mill and a chlor-alkali plant producing about 45 tons of chlorine per day. Both facilities are owned by Reed Limited, Pulp and Paper Group. The chlor-alkali plant utilized a mercury cell process from 1962 until late 1975, when membrane cells were installed. Potential air pollutants associated with the pulp mill would include sulphur dioxide, soot, fly-ash and other particulate matter from power boilers; hydrogen sulphide, other gaseous organic sulphides, sodium sulphate and sodium carbonate from the chemical recovery process; sodium and calcium salts from the lime kiln; and chlorine and chlorine dioxide from the bleaching operation. Mercury (until late 1975) and chlorine could also be emitted from the chemical plant. Minor additional sources would include sawdust from chip piles and dust stirred up by movement of trucks and other equipment.

Air quality investigations in the Dryden area began in 1970, when atmospheric mercury concentrations were assessed at a mercury disposal site, about 5 kilometres west-northwest of Dryden. This survey was repeated in 1971. In 1972, a preliminary vegetation and soil sampling study was carried out in the vicinity of the pulp mill. This work was again undertaken, with modifications, in 1975.

Dustfall and sulphation rate monitoring began in 1973 at one location about 1000 metres east-northeast of the kraft mill. Five additional dustfall sites were added in late 1975, and sulphation rates were also measured at three of these.

Supplementary information was obtained from snow sampling surveys in early 1974 and 1975, which yielded data on the nature, quantity and distribution of contaminants in snow near the pulp mill.

Measurements of atmospheric concentrations of sulphur dioxide, mercury, hydrogen sulphide and suspended particulate were made in July, 1975, by a mobile monitoring unit supplied by Air Resources Branch, Toronto.

VEGETATION AND SOIL ASSESSMENT

In August, 1972, samples of soil (0-5 centimetre depth), moss (*Hypnum* spp.), white spruce foliage and trembling aspen foliage were collected from each of seven sites, plus one control, for mercury analysis. At the same locations, plus four additional sites, white spruce and trembling aspen foliage, forage (grass) and soil (0-10 cm) were sampled for analysis of chloride, fluoride, iron, sodium and sulphur content. The July, 1975, survey was modified to include 12 sample sites, plus two controls, with most sites being located close to the source under investigation. Only trembling aspen foliage and two depths of soil (0-5 cm, 5-10 cm) were sampled, and all material was analysed for chloride, mercury and sodium. In a supplementary survey in October, 1975, soil for mercury analysis was collected from eight locations not previously sampled. The distribution of 1972 and 1975 vegetation and soil sampling points are shown in Figure 1. During the October survey, samples of spruce bark from the company's wood storage area near the mill were collected for mercury determination.

(a) Mercury

Mercury levels in vegetation and soil collected in 1972 and 1975 are summarized in Table 1. Comparison between results from the two surveys is difficult because of differences in sample sites, sample processing methods and analytical techniques. Values for moss are also suspect because of possible contamination by adhering soil particles. The 1975 trembling aspen results showed a trend of decreasing mercury concentrations with distance from the mill area, but the centre of greatest contamination was north of the kraft mill (Figure 2). In contrast, mercury content in soil was highest near the chemical plant (Figures 3 and 4) and there was a gradient of decreasing concentrations with increasing distance from this area. Surface soil contained more mercury than the subsurface layer, suggesting that contamination was airborne. No criteria or standards have been established for mercury in vegetation or soil.

Five samples of spruce bark from wood piled near the mill contained low concentrations of mercury. Although bark from wood at the bottom of the oldest piles contained more mercury than bark from wood at the top of more recent piles, all mercury levels were less than 0.1 ppm.

(b) Other Contaminants

Results from chloride and sodium analysis of vegetation and soil are presented in Table 2. Although chloride content in trembling aspen foliage was often higher in the survey area than at control sites, especially in 1975, there was no definite indication of a concentration gradient in the kraft mill area. Excessive sodium concentrations in vegetation occurred only at two locations sampled in 1972. Foliar values for 1975 were higher near the mill than at control sites, but no concentration gradient was apparent. Sodium levels in soil were fairly uniform in 1972, but a clear pattern of decreasing concentration with distance was evident in soils collected in 1975. Iron, fluoride and sulphur levels, from the 1972 survey, were uniformly low in all sample material.

SNOW SAMPLING

Snow samples were obtained from 17 sites in early 1974 and 26 locations in early 1975. Results of both surveys, reported earlier, demonstrated the presence of significantly elevated levels of calcium, sodium and sulphate in snow collected near the mill and in the adjacent town area. A small area of snow contaminated by mercury was detected near the chemical plant and pulp mill. Calcium levels were highest near the lime kiln and concentrations of this element tended to increase through the winter. Variations in the pH of snow meltwater seemed to be most closely associated with changes in calcium concentration. Visible contamination of snow by grey and black coloured particulate matter was observed up to 2000 metres north, 1000 m east and 500 m south of the kraft mill. Sawdust and particles of bleached kraft were noted on snow up to 500 m east

and 250 m south of the mill.

AIR MONITORING

(a) Dustfall

Dustfall is one of the most visible classes of air pollutants. It comprises particulate matter which settles out from the atmosphere under the influence of gravity. It is measured by exposing open-top vessels for 30 days and weighing the collected matter. Results are expressed in tons per square mile per month.

Dustfall sampling locations in Dryden are shown in Figure 5. The only results available prior to 1975 were collected at station 61004, about 1000 metres east of the kraft mill. Dustfall measurements at this site are given in Table 3. Although most values were well over the criterion, it was felt that much of the dust could be attributed to re-entrainment from nearby sources. For this reason, the station was moved to a more suitable site (61020) in late 1975. For the six present stations, only three months of data were collected in 1975 and these are summarized in Table 4. No conclusions can be reached at this time.

(b) Sulphation Rate

Sulphation rate is measured by exposing lead dioxide plates to the air for 30-day periods. Lead dioxide reacts with sulphur compounds in the atmosphere to form lead sulphate. Results are expressed in milligrams of sulphur trioxide per hundred square centimetres per day (mg SO_3/100 cm^2/day). Because of its oxidizing power, lead dioxide also converts other reactive sulphur compounds, such as hydrogen sulphides and mercaptans, into sulphate. In Dryden, where sulphur dioxide levels have been found to be low (see following section of report), lead dioxide plates are being used primarily as detectors of hydrogen sulphide and other organic sulphide compounds.

Sulphation monitoring sites are designated in Figure 5 and measured values are shown in Tables 3 and 4. At the oldest station

(61004), 1000 metres from the source, sulphation rates were low at all times (Table 3). The limited data available from closer points (Table 4) indicates that much higher sulphation rates can be expected near the kraft mill.

(c) Source Monitoring Survey

An air quality survey was carried out in late July by a mobile van unit from Air Resources Branch, Toronto. Depending on wind direction and accessibility, monitoring usually began downwind of the source at the point of expected highest pollutant concentration. Measurements of gaseous pollutants (sulphur dioxide, mercury and hydrogen sulphide) were then made for periods of at least 30 minutes. Suspended particulate concentrations were determined using standard high volume samplers operated for 24-hour periods.

(i) Sulphur Dioxide

Sulphur dioxide was monitored for 5 hours, 10 minutes at sites 1 and 4 (Figure 6). All concentrations were very low and the maximum 30-minute average did not exceed 0.02 ppm, well below the standard of 0.3 ppm.

(ii) Mercury

Over 19 hours of data on atmospheric mercury levels were collected in Dryden and 3 hours, 36 minutes of measurements at the mercury disposal site west of the town. These data are summarized in Tables 5 and 6. Highest half-hour averages were encountered at sites 6 and 7, closest to the chemical plant, but the Ontario standard (5000 nanograms per cubic metre) was not exceeded.

At the mercury disposal site, averages above the provincial standard were monitored on July 28 (Table 6). Highest values were found only in the immediate vicinity of an open trench containing waste material from the chemical plant (Figure 7). Mercury levels were below the standard near covered disposal sites. Concentrations in

1975 were similar to those recorded in 1970 and 1971.

(iii) Hydrogen Sulphide

Hydrogen sulphide was monitored at all sites in Dryden (Figure 6), yielding 27 hours, 33 minutes of data (Table 7). The Ontario standard (20 ppb) was exceeded at all locations. Concentrations at more distant points (sites 10 to 15) were generally lower than those closer to the mill. Highest hydrogen sulphide levels were recorded at site 1, where vapors rising from the Wabigoon River probably accounted for much of the concentration monitored. An example of plotted running averages is shown in Figure 8 for site 8.

(iv) Suspended Particulate

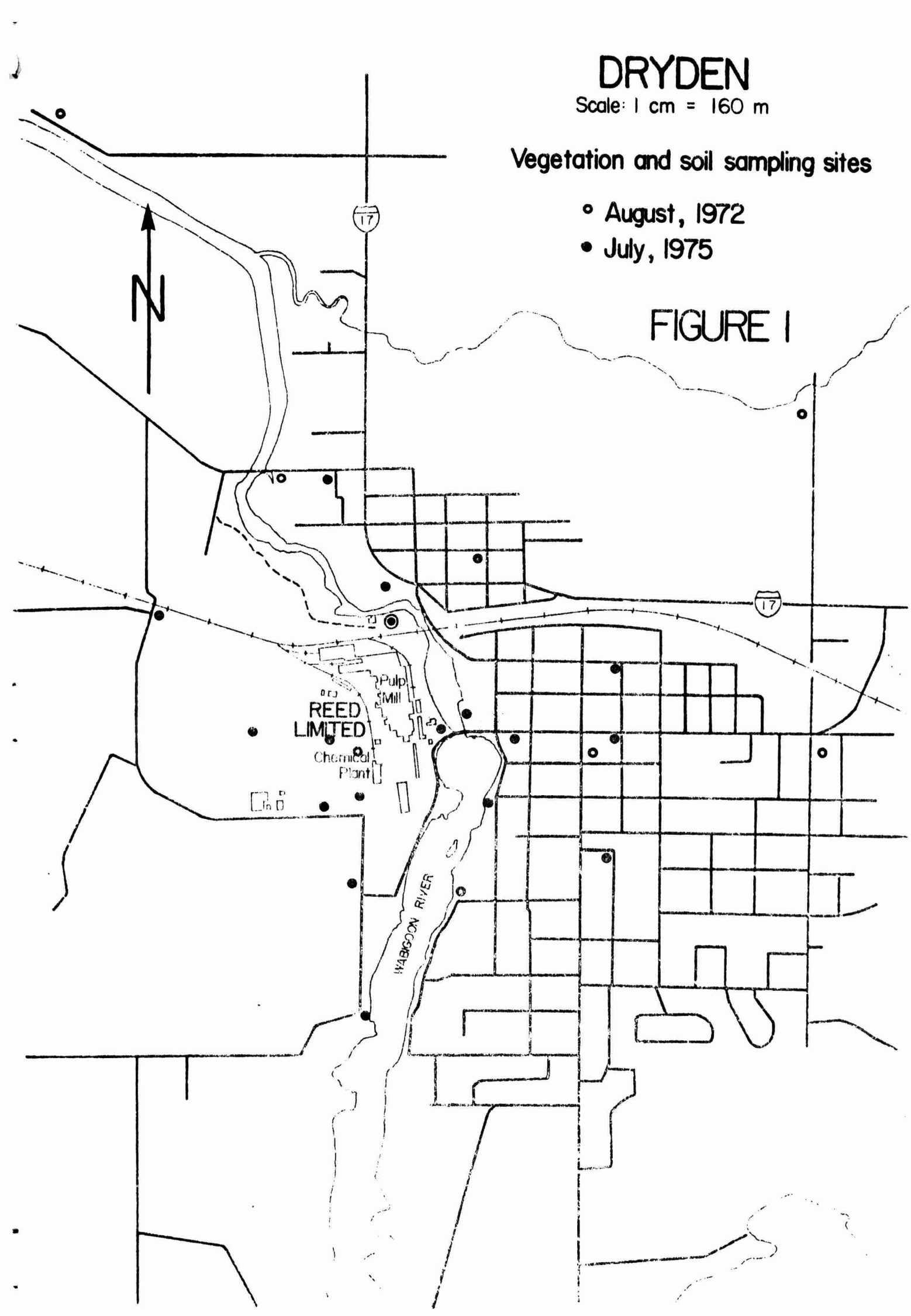
Suspended particulate constitutes particulate matter of small size which remains in the atmosphere for extended periods. A known volume of air is drawn through pre-weighed glass fibre filters for 24-hour periods and the filters are then re-weighed to determine the quantity of dust collected. Results are expressed in micrograms per cubic metre of air ($\mu g/m^3$). Dryden filters were also analysed to determine content of calcium, sodium and sulphate.

Monitoring sites are shown in Figure 9 and results in Table 8. The 24-hour standard (100 $\mu g/m^3$) was exceeded in five of 12 samples, but insufficient information was collected to establish a gradient of decreasing concentrations with increasing distance from the kraft mill. Analysis of filters showed no relationship between total suspended particulate levels and concentrations of calcium, sodium or sulphate.

ACKNOWLEDGEMENTS

Contributions and assistance from the following agencies is gratefully acknowledged:

- Air Quality Laboratory Section, Laboratory Branch, for chemical analysis of vegetation and soil and for preparing and analysing sulphation plates.
- Regional Laboratory, Northwestern Region, for dustfall weight determinations and for chemical analysis of snow meltwater.
- Inorganic Trace Contaminant Section, Laboratory Branch, for mercury analysis of snow meltwater, soil and bark, and for conducting the October soil and bark sampling program.
- Instrumentation Development and Monitoring Unit, Technology Development and Appraisal Section, Air Resources Branch, for conducting the July air quality survey.
- Phytotoxicology Section, Air Resources Branch, for technical advice and for processing vegetation and soil samples.
- Industrial Abatement Section, Kenora District Office, for assistance with snow sampling.

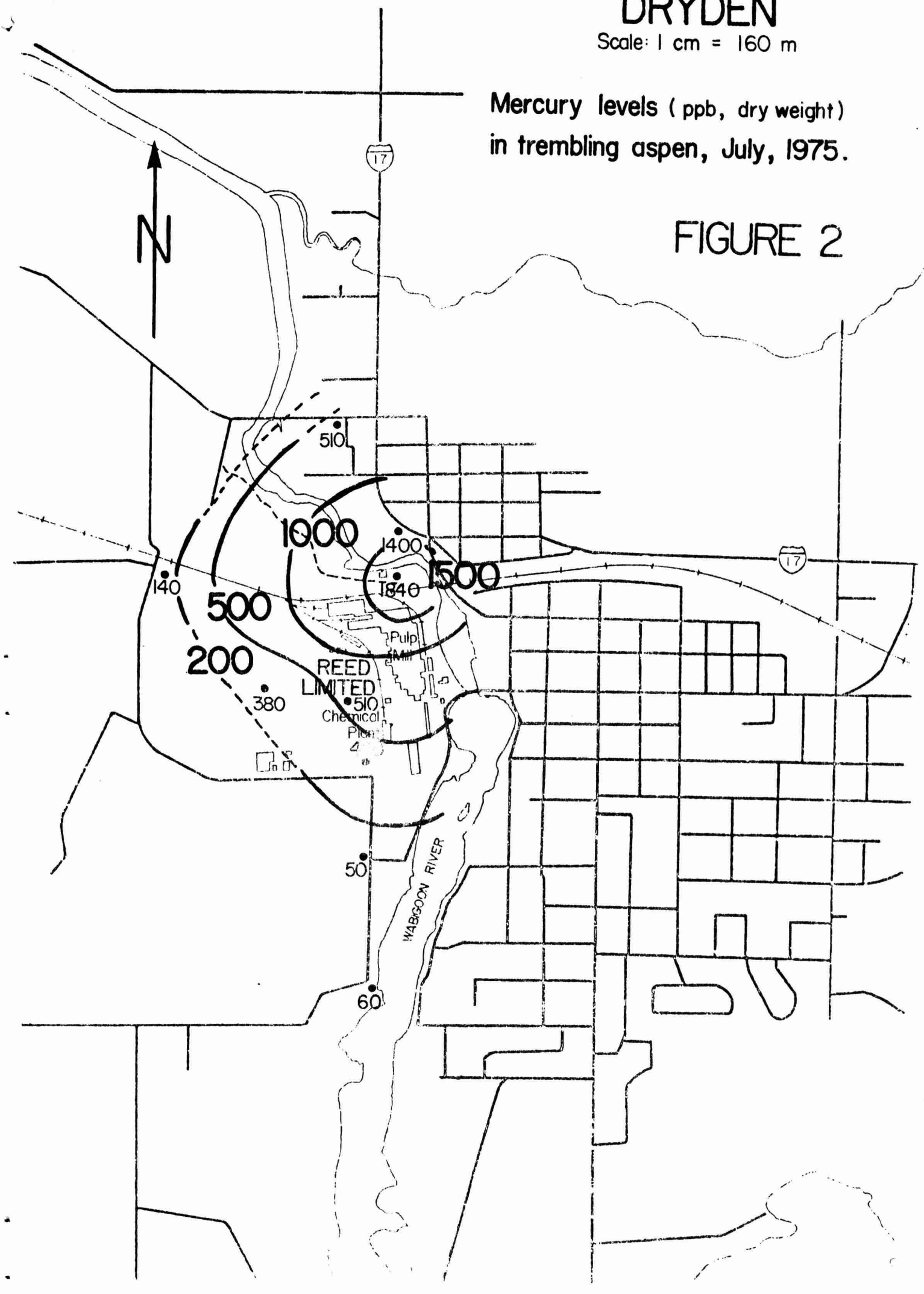

DRYDEN
Scale: 1 cm = 160 m
Vegetation and soil sampling sites
° August, 1972
• July, 1975
FIGURE 1
N
17
17
Pulp Mill
REED LIMITED
Chemical Plant
WABIGOON RIVER

DRYDEN

Scale: 1 cm = 160 m

Mercury levels (ppb, dry weight) in trembling aspen, July, 1975.

FIGURE 2



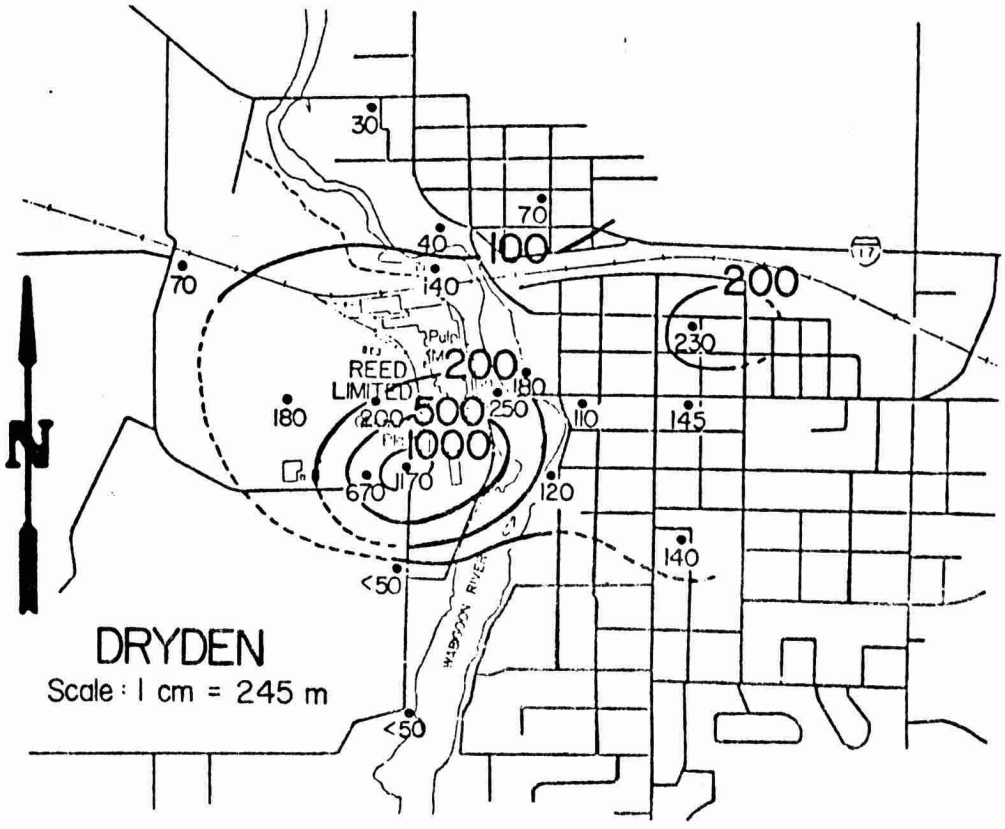


FIGURE 3 Mercury levels (ppb, dry weight) in soil (0-5 cm), July, 1975.

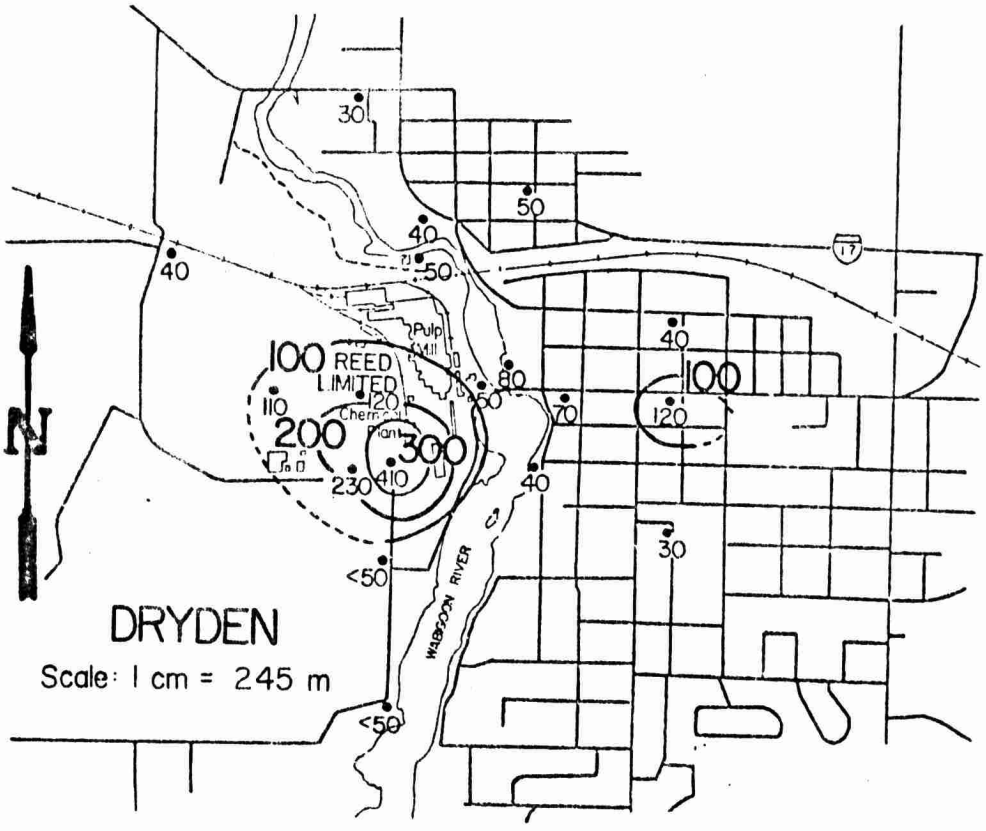
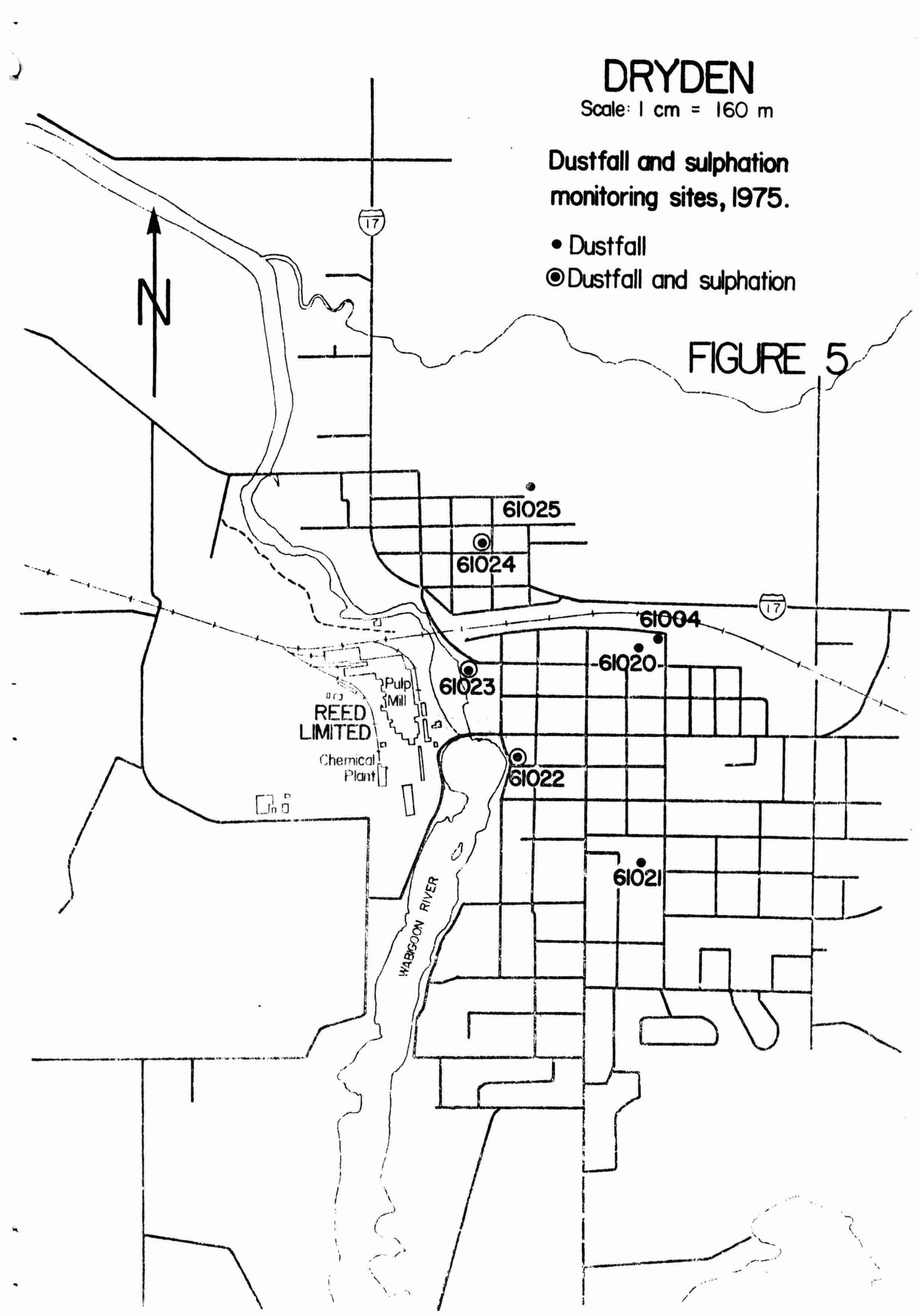
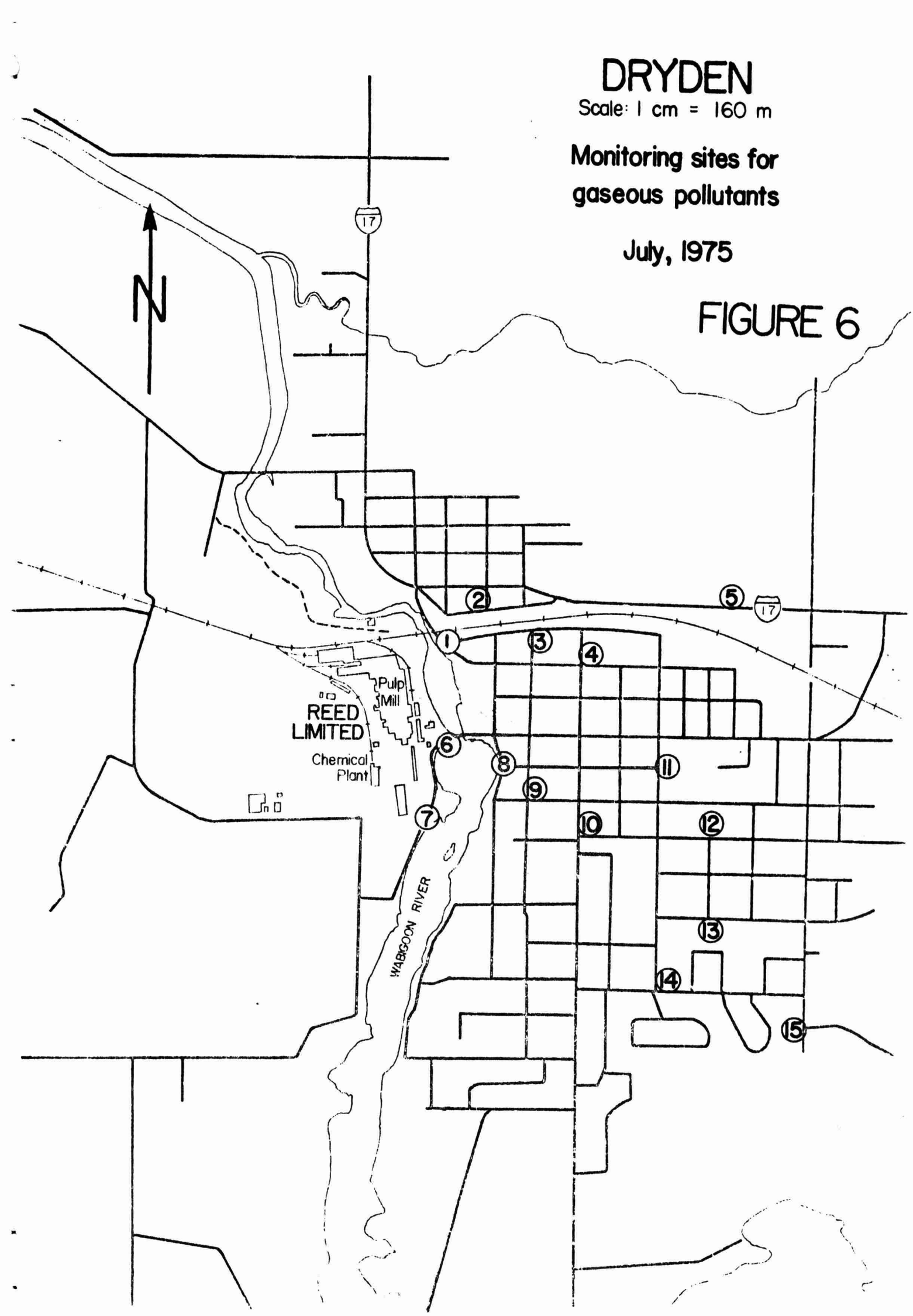


FIGURE 4 Mercury levels (ppb, dry weight) in soil (5-10 cm) July, 1975.


DRYDEN
Scale: 1 cm = 160 m
Dustfall and sulphation monitoring sites, 1975.
• Dustfall
◉ Dustfall and sulphation
FIGURE 5
N
17
61025
61024
61004
61020
61023
Pulp Mill
REED LIMITED
Chemical Plant
61022
61021
WABIGOON RIVER


DRYDEN
Scale: 1 cm = 160 m
Monitoring sites for gaseous pollutants
July, 1975
FIGURE 6
N
17
REED LIMITED
Pulp Mill
Chemical Plant
WABIGOON RIVER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

CONCENTRATION VS TIME

FIGURE 7

SURVEY: DRYDEN #25
DATE: JUL 28 1975
SCAN TIME: 22 SEC
STANDARD: 5 UG/M3
LOCATION: DRYDEN CHEMICAL HG DUMP SITE

POLLUTANT: HG
START TIME: 12:38
AVERAGING TIME: 30 MIN
DISTANCE: 0.2KM, 2DEG FROM DUMP

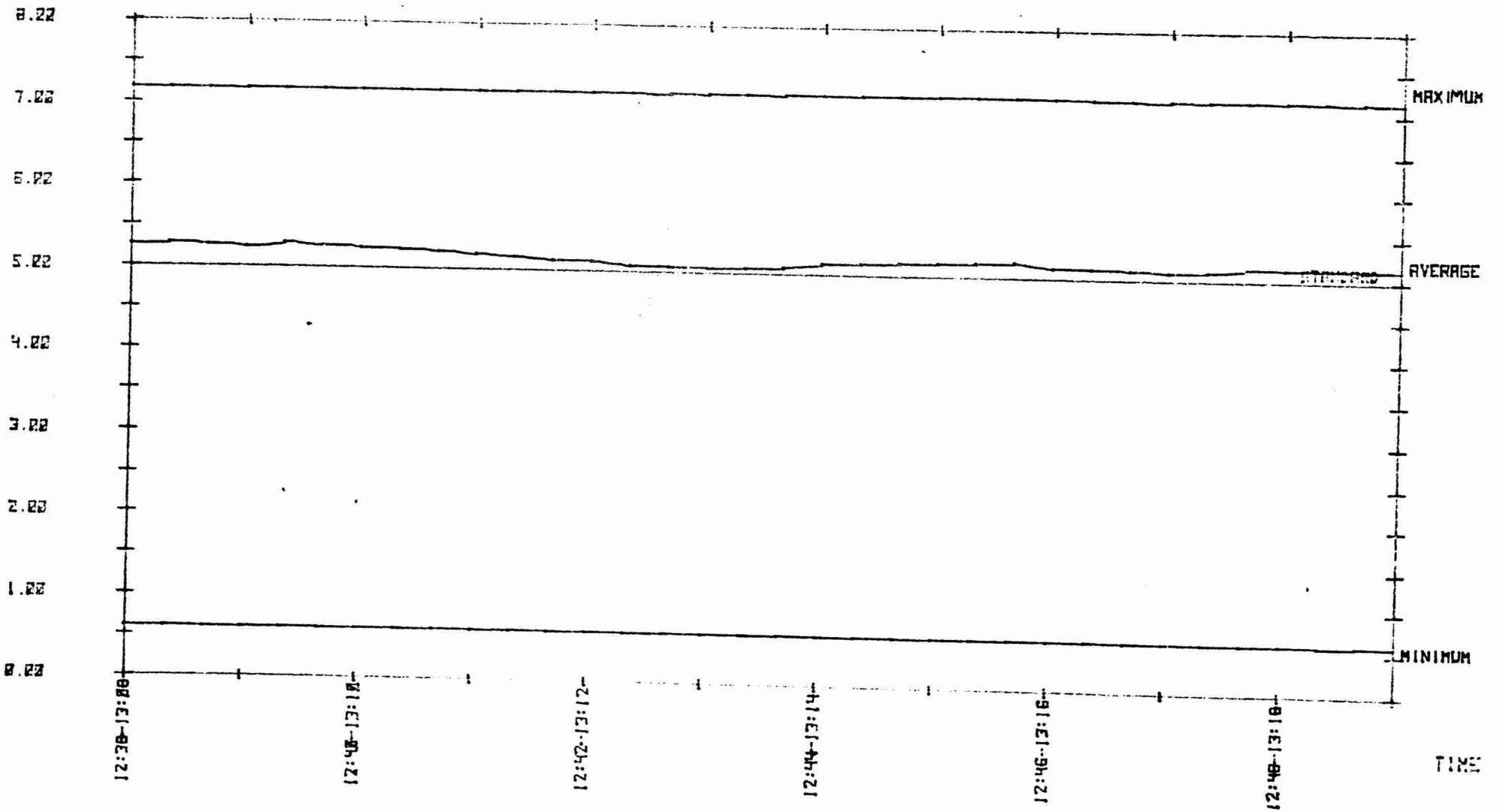
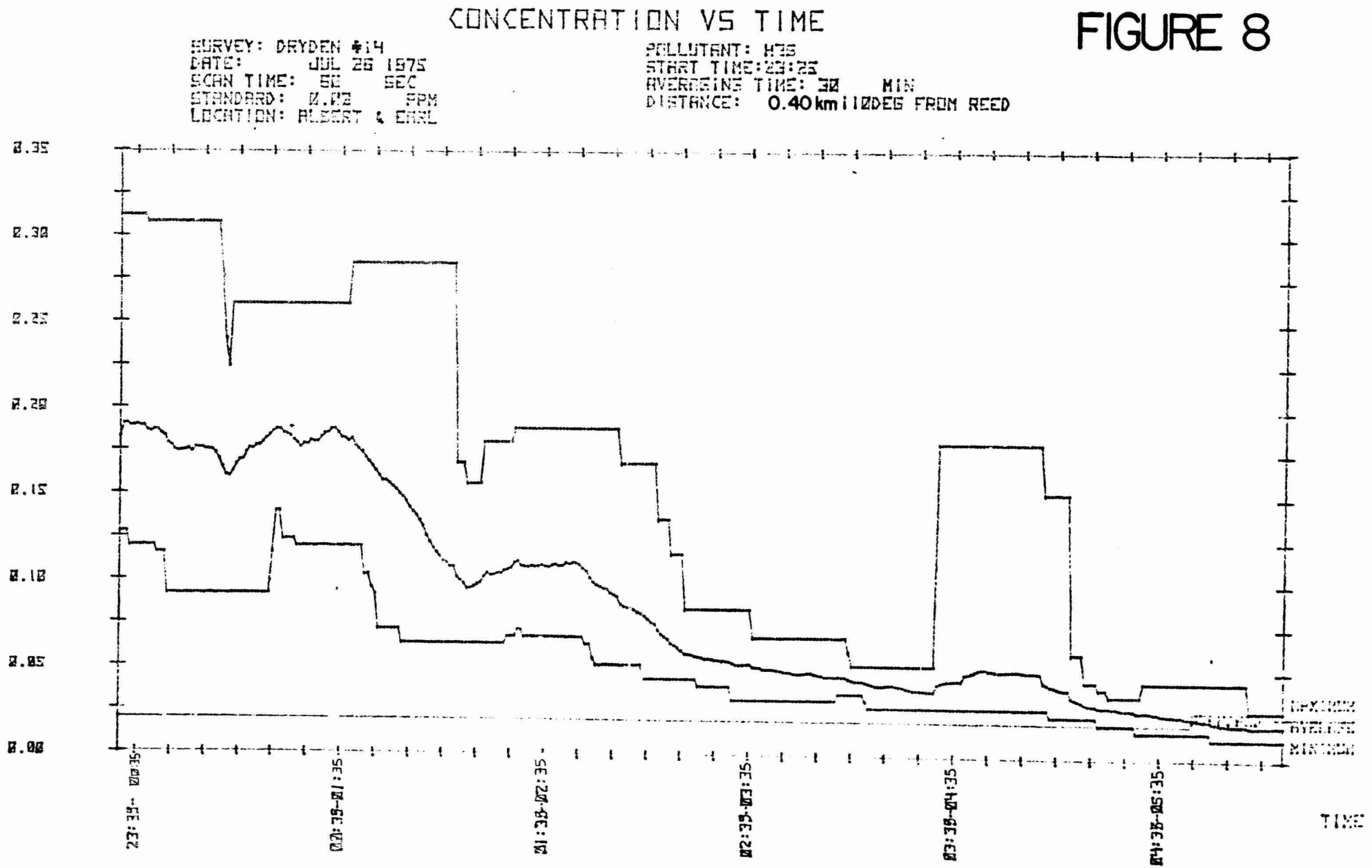


FIGURE 8


CONCENTRATION VS TIME
SURVEY: DRYDEN #14
DATE: JUL 26 1975
SCAN TIME: 60 SEC
STANDARD: 0.02 PPM
LOCATION: ALBERT & EARL
POLLUTANT: H2S
START TIME: 23:25
AVERAGING TIME: 30 MIN
DISTANCE: 0.40 km 100DEG FROM REED
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
CONCENTRATION H2S PPM
23:35- 00:35
00:35-01:35
01:35-02:35
02:35-03:35
03:35-04:35
04:35-05:35
TIME

DRYDEN

Scale: 1 cm = 160 m

Monitoring sites for suspended particulate

July, 1975

FIGURE 9

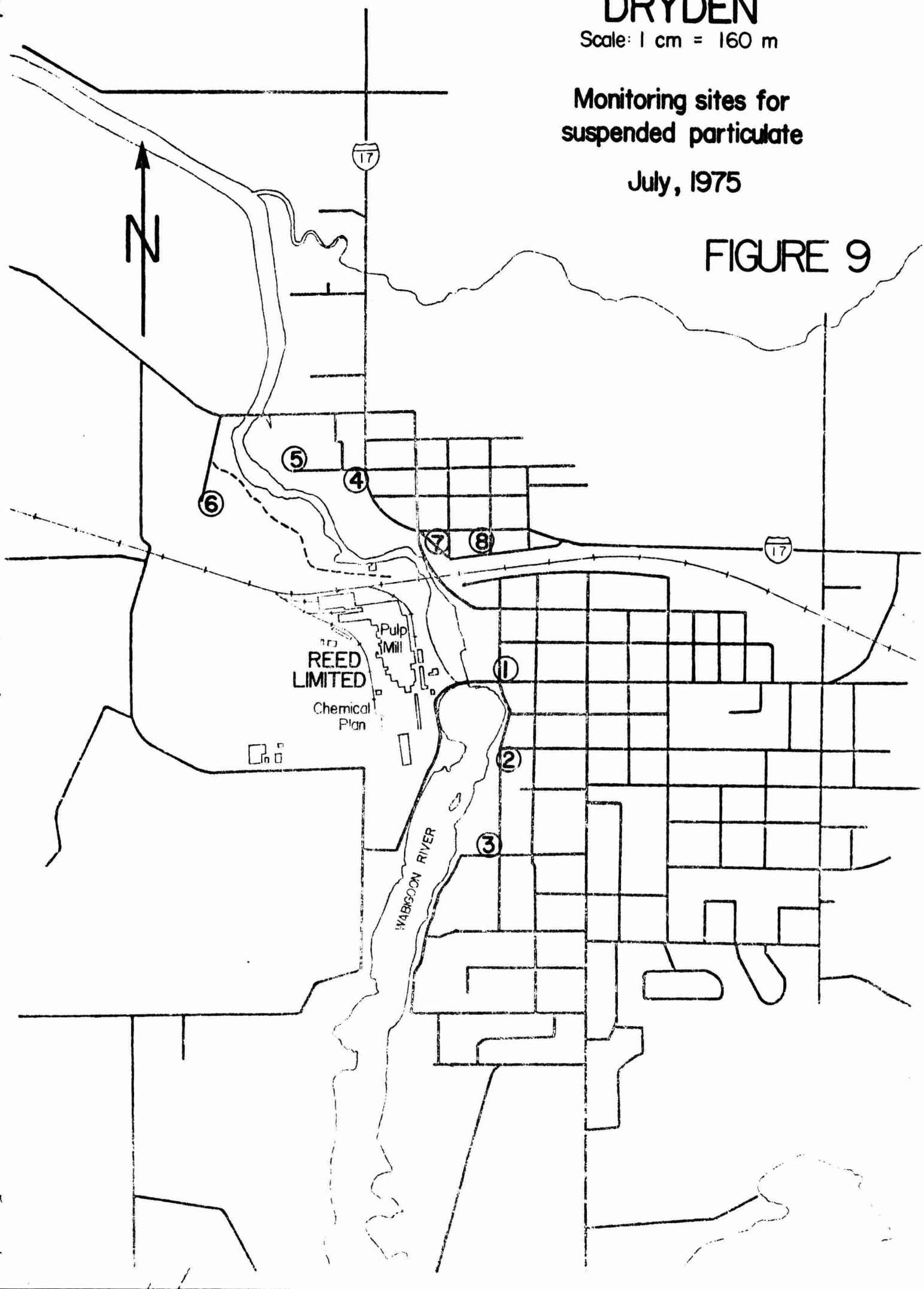


TABLE 1. Mercury concentrations (ppb, dry weight) in vegetation and soil, Dryden, 1972 and 1975.

Distance(metres) and direction from source*	Trembling aspen		Moss	Soil		
				1972	1975	
	1972	1975	1972	0-5 cm	0-5 cm	5-10 cm
550 N	92	1840	3460	6650	140	50
700 N		1400			40	40
1105 N	< 5	510	72	130	30	30
2600 NNW	16		110	130		
270 NE					250	50
405 NE					180	80
880 NNE					70	50
2000 NE	< 5		210	100		
520 ENE					110	70
880 E	35		150	31	145	120
960 ENE					230	40
350 ESE					120	40
530 SE	62		110	34		
900 ESE					140	30
110 SW		460			1170	410
230 SW					670	230
425 SSW		50			< 50	< 50
880 S		60			< 50	< 50
220 NW		510			200	120
480 WNW		380			180	110
975 WNW		140			70	40
Controls:						
32.0 km E	9		53	190		
7.7 km ENE		< 20			< 50	< 50
10.7 km WNW		< 20			< 50	< 50

*Source designated as centre of Reed Limited chemical plant.

TABLE 2. Concentrations of chloride and sodium (ppm, dry weight) in trembling aspen and soil at Dryden, 1972 and 1975.

Distance(metres) and direction from source*	Chloride		Sodium				
	Trembling aspen		Trembling aspen		Soil		
	1972	1975	1972	1975	1972 0-10cm	1975 0-5cm	1975 5-10cm
100 NNW	1400		11500		250		
550 N	2500	2500	2500	165	500	685	660
700 N		1300		145		580	610
1105 N	1000	2800	57	140	250	325	390
2600 NNW	1100		104		375		
4800 NNW	2000		344		425		
270 NE						345	280
2000 NE	700		200		250		
3200 NE	4100		200		200		
520 ENE						635	545
880 E	3500		321		225	245	280
1600 E	2300		275		250		
530 SE	7500		200		350		
110 SW		2100		190		380	315
425 SSW		1600		100		195	230
880 S		1600		110		950	765
220 NW		1700		95		1075	1040
480 WNW		2700		155		860	530
975 WNW		1200		105		360	355
Controls:							
32.0 km E	1300		445		375		
7.7 km ENE		600		20		315	335
10.7 km WNW		300		20		155	140

*Source arbitrarily designated as recovery furnace stack, Reed Limited kraft pulp mill.

TABLE 3. Levels of dustfall and sulphation rate at station 61004, Dryden, for 1973-1975.

Month	Dustfall (tons/sq. mile/30 days) 1973	1974	1975	Sulphation Rate (mg SO_3/100 cm^2/day) 1973	1974	1975
January	27*	4	12	.08	.02	.04
February	25	-	10	.04	.02	.04
March	22	20	22	.07	.01	.06
April	32	35	30	.09	.02	.02
May	32	38	24	.07	.10	.03
June	50	75**	33	.12	-	.04
July	57	75**	34	-	.06	.13
August	41	32	27	.05	.09	.16
September	40	33	7	.14	.05	.03
October	28	26**	-	.14	.07	.07
November	15	26**	-	.07	.04	-
December	-	7	-	.07	.04	-
Mean	34	30	22	.09	.05	.06

*Values exceeding criterion of 20 (monthly) or 13 (annual average) are underlined.

**Two-month exposure periods (June-July, October-November).

TABLE 4. Dustfall and sulphation rate, Dryden, October-December, 1975.

Station	Location	Distance (metres) and direction from source*	Dustfall (tons/sq. mile/30 days)			Sulphation (mg SO_3/100 cm^2/day)		
			Oct.	Nov.	Dec.	Oct.	Nov.	Dec.
61024	Mary/Florence	735 NNE	15	16	35	.15	.23	.09
61025	Park/Second	960 NNE	-	29	11			
61023	King/Wabigoon R.	305 NE	26**	28	20	.46	.27	.17
61020	Kirkpatrick/Queen	895 ENE	19	18	9			
61022	Earl/Albert	430 ESE	15	24	15	.18	.21	.14
61021	Casimir/St. Charles	1010 ESE	-	14	14			

*Source arbitrarily designated as recovery furnace stack, Reed Limited kraft pulp mill.

**Values exceeding monthly criterion of 20 are underlined.

TABLE 5. Atmospheric mercury concentrations monitored in Dryden, July, 1975.

Site	Date	Period monitored	Concentrations (ng/m^3)* 30-minute averages Min.	30-minute averages Max.	Peaks Min.	Peaks Max.
2	July 25	21:45-22:56	28	150	0	329
5	" 26	08:47-09:16	0	0	0	0
8	" 26	09:40-11:15	190	320	0	1460
	" 26	17:23-17:56	3	4	0	26
	" 26-27	23:25-05:35	0	330	0	696
9	" 26	11:21-12:21	39	130	0	366
10	" 26	12:30-13:00	130	130	60	206
6	" 26	13:52-15:23	45	260	25	1070
7	" 26	15:35-16:05	160	160	25	1210
	" 26	16:17-17:18	830	920	174	1880
	" 27	13:42-15:13	590	730	91	1890
1	" 26	21:37-22:10	0	0	0	0
	" 27	15:28-17:58	34	640	10	3560

*ng/m^3 - nanograms per cubic metre (1 ng/m^3 = 0.001 $\mu g/m^3$).

TABLE 6. Atmospheric mercury concentrations monitored at Reed Limited mercury disposal site, Dryden, July, 1975.

Date	Period monitored	Concentrations (ng/m^3) 30-minute averages Min.	30-minute averages Max.	Peaks Min.	Peaks Max.
July 28	10:05-10:53	1200	1400	292	6220
" 28	11:16-12:17	2800	4600	437	7130
" 28	12:38-13:18	5100	5300	603	7160
" 28	13:52-14:59	1800	3700	462	7130

TABLE 7. Hydrogen sulphide levels monitored in Dryden, July, 1975.

Site	Date	Period monitored	Concentrations (ppb) 30-minute averages Min.	30-minute averages Max.	Peaks Min.	Peaks Max.
1	July 25	21:00-21:38	140	180	74	351
	" 26	21:37-22:10	950	1000	590	2370
	" 26	22:12-23:18	590	700	412	1130
	" 27	15:28-17:58	37	220	24	1050
2	" 25	21:45-22:57	140	210	82	382
3	" 25	20:20-20:54	120	140	74	351
4	" 28	15:58-16:50	76	150	31	518
	" 28	17:26-19:04	51	210	30	438
5	" 26	08:47-09:16	46	46	9	108
6	" 26	13:52-15:23	160	410	92	1120
7	" 26	15:35-16:05	61	61	43	132
	" 26	16:17-17:18	33	51	27	225
	" 27	13:42-15:13	31	92	11	346
8	" 26	09:40-11:15	140	220	72	775
	" 26	17:23-17:56	380	410	143	866
	" 26-27	23:25-05:35	19	190	12	312
9	" 26	11:21-12:21	230	500	125	1140
10	" 26	12:30-13:00	130	130	75	291
11	" 27	06:30-08:05	4	21	0	300
12	" 27	08:21-08:49	140	140	64	243
13	" 27	08:58-09:28	120	120	65	205
14	" 26	13:06-13:36	59	59	45	108
15	" 27	10:37-11:04	51	56	30	114

TABLE 8. Suspended particulate in Dryden, July, 1975.

Site	Distance (metres) and direction from source*	Date	Suspended particulate ($\mu g/m^3$)
1	380 E	July 27	232
		" 28	155
2	480 SE	" 27	94
		" 28	130
3	670 SSE	" 27	23
		" 28	44
4	690 NNW	" 29	99
		" 30	77
5	800 NNW	" 29	89
6	930 NW	" 29	60
7	480 NNE	" 30	187
8	575 NNE	" 30	253

*Source arbitrarily designated as recovery furnace stack, Reed Limited kraft pulp mill.